



Highly proton-conductive thermally rearranged polybenzoxazole for medium-temperature and low-humidity polymer electrolyte fuel cells



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HIGHLIGHTS

- Acid doped thermally rearranged polybenzoxazole membranes for medium temperature fuel cell.
- Cavity control in TR-PBO membrane impregnates acid dopants.
- Doped TR-PBO results in fast proton conduction behavior and excellent tolerance to acid leaching.

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ABSTRACT

Here a new membrane design concept to improve proton conductivity and to maintain a constant acid doping level for an extended period of time for medium-temperature and low-humidity polymer electrolyte fuel cells (MT/LH-PEFC) is presented. A polymer electrolyte membrane is prepared via thermal rearrangement of hydroxyl-containing polyimide (HPI) precursor membranes over 350 °C, followed by subsequent acid-impregnation. The thermal treatment for 1 h converts HPI into a thermally rearranged polybenzoxazole (TR-PBO) membrane with high surface area, similar to zeolites. The microporous structure and the basic sites ($-C=N-$) in benzoxazole moieties contribute to the stable impregnation of small acidic molecules (e.g., HCl, HNO₃, H₃PO₄, and HPF₆) in large quantities within the polymer matrix. The acid-doping level decreases with the increasing size of acidic dopants. TR-PBO impregnated using HCl with the smallest radius has a much higher doping level and excellent proton conductivity ($1.60 \times 10^{-1} \text{ S cm}^{-1}$ at 130 °C and RH 28%) when compared with PBI ($6.59 \times 10^{-2} \text{ S cm}^{-1}$ at the same conditions). Different from a common acid-doped PBI system, the acid-doped TR-PBO membranes do not exhibit a severe acid leaching even in repeated heating and cooling cycles between 90 and 130 °C.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) have been perceived as a promising electrochemical device producing renewable energy with high efficiency [1]. Among them, the medium-temperature and low-humidity PEFCs (MT/LH-PEFCs) operate in a dry state under a temperature range between 120 and 180 °C. MT/LH-PEFCs have a variety of advantages such as relatively fast kinetics of electrode reaction, better heat utilization, favorable integration of fuel processing units, and improved resistance to carbon monoxide (CO) poisoning onto platinum (Pt) catalyst [2].

There have been great efforts to develop desirable polymer electrolytes for MT/LH-PEFCs. One approach is to fabricate sulfonated polymer-inorganic composites containing hygroscopic inorganic oxides [3,4] and heteropolyacids [5–8] in order to enhance water retention levels and to compensate proton conductivity reduced as a result of membrane dehydration at a temperature higher than 100 °C, respectively. Another is to replace water molecules as proton transport media in sulfonated polymers with non-aqueous and low-volatile heterocyclic compounds (e.g., imidazole and imidazolium salt, pyrazole, and benzimidazole solution) [9–11]. Both membrane materials, however, are still not free from severe losses in proton conduction in conjunction with thermal decomposition of their sulfonic acid groups [12].

The most successful MT/LH-PEFC membrane study is observed in the impregnation of strong inorganic acids (e.g., phosphoric acid (H₃PO₄) [13–16], hydrochloric acid (HCl) [17], and nitric acid

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(HNO₃) [17] into basic polymers bearing electron-donating groups (e.g., ether, alcohol, imine, amide, or imide). The basic polymers form hydrogen bonds with the acids which undergo spontaneous dissociation to some extent even under water-free conditions. The self-ionization enables protons to be transported in the acid-doped polymers [18]. A representative acid-doped polymer is poly-benzimidazole (PBI, pK_a = ~5.5) impregnated with H₃PO₄ in which two protons per repeating unit delocalize its electron density for forming a stable polymer system through the resonance stabilization [19]. The acid–base complexation is made by treating PBI in the membrane state with highly concentrated H₃PO₄ solution for a given time [9,13–17] or by polymerizing PBI in polyphosphoric acid used as both a solvent and a dopant [20–23]. In spite of much effort, it is still difficult to meet electrochemical performance requirements owing to their relatively low proton conductivities (e.g., $<4 \times 10^{-2} \text{ S cm}^{-1}$) under MT/LH-PEFC operation conditions. The PBI membranes, particularly with high H₃PO₄ contents, also suffer from the acid leaching; the dopants leach out with a small amount of water molecules produced as a result of the redox reaction. It hinders the MT/LH PEFC system from exhibiting a high technical reliability for an extended period of time.

This paper describes a new membrane material design concept to improve proton conduction capability and to minimize severe acid leaching by controlling characteristics of cavities in the polymer matrix, which are believed to be used as acid reservoirs. Polybenzoxazole (PBO) was employed as a polymer matrix for doping acids. PBO has excellent thermal and chemical stability, and good hydrolytic resistance. When treated with acids, the basic polymer forms ionic complexes in the form of counter anions bound to its protonated benzoxazole groups in which protons are mainly located on its nitrogen atoms, maintaining the same distance as the usual N–H bond length in the orientation bisecting the –C=N–C– bond angle on the heterocyclic rings. Different from conventional PBO synthesized by polycondensation reaction of a bis-aminohydroxyphenyl compound and a dicarboxylic acid, microporous PBO (TR-PBO) used in this study was prepared from hydroxyl-containing polyimide (HPI) precursor in the membrane state via thermal rearrangement reaction over 350 °C [24]. The resulting TR-PBO membranes exhibited a large surface area over HPI precursor. The cavity in TR-PBO was narrowly distributed in bimodal shape with the mean size of about 3.8 Å and 9 Å. The connectivity of the cavity was much improved after the thermal rearrangement [25]. Here, it was noticed that the small cavity size of the basic polymer is similar to thermodynamic diameters of acidic dopants and the cavities are connected each other. It means that a large portion of the dopants may exist in the cavities stably regardless of water generation during MT/LH-PEFC operation and the cavity network may be utilized as an effective proton transport pathway, respectively.

The goal of this study is to systematically investigate acid-doping effects on basic polymer matrices from HPI precursor to TR-PBO prepared under different thermal protocols. The ultimate objective of this study is to disclose the importance of cavity characteristics for both proton conduction and the acid preservation. Finally, thermo-oxidative resistance and electrochemical reliability of acid-doped TR-PBO membranes were observed under thermal aging histories and during repeated heating and cooling cycles, respectively.

2. Experimental

2.1. Materials

2,2-Bis(3-amino-4-hydroxy-phenyl)hexafluoropropane (APAF, FW = 366.26 g mol^{−1}) as a diamine was purchased from Tokyo

Kasei Co., and used as received. 4,4-(Hexafluoroisopropylidene)diphthalic anhydride (6FDA, 99 wt.%, FW = 444.24 g mol^{−1}) and 1-methyl-2-pyrrolidinone (NMP, anhydrous) were purchased from Aldrich Chemical Co. (WI, USA), and used as a dianhydride and a solvent, respectively. Hexafluorophosphoric acid (HPF₆), HCl, HNO₃, and H₃PO₄ (Aldrich Chemical Co., WI, USA) were purchased, and used as dopants.

2.2. Synthesis of polyimide precursor (HPI), and membrane formation

HPI precursor was synthesized via thermal imidization following synthetic procedures in Fig. 1 [24,25]. APAF (10 mmol) with hydroxyl functional groups was dissolved in NMP solution under a nitrogen atmosphere using mechanical stirrer, until a clear solution was obtained. 6FDA in the powder state was slowly added into APAF solution. The reaction mixture was stirred for one day at ambient temperature to yield a transparent viscous poly(amic acid) (HAA) solution. Then, HPI membrane was prepared by casting HAA solution onto the glass plate and thermally treating in vacuum with stepwise imidization protocols: 100 °C for 1 h, 150 °C for 1 h, 200 °C for 1 h, and 250 °C for 1 h. After imidization, the vacuum oven was cooled to ambient temperature.

2.3. Preparation of thermally rearranged polybenzoxazole (TR-PBO) membranes

TR-PBO membranes were fabricated from HPI in the membrane state via the thermal rearrangement (see Fig. 1). Prior to the thermal treatment, the membrane samples were dried at 110 °C in vacuum to remove any residual NMP, water molecules, and dust. For thermal rearrangement, HPI membrane on an alumina holder plate was placed in the middle of a quartz tube of the muffled tubular furnace where argon gas flowed at a rate of 150 ml min^{−1}. An isothermal annealing was carried out at 300 °C for 1 h to finish thermal imidization. Then, the HPI membrane was thermally treated at three different temperatures (350, 400, and 450 °C) for 1 h. The furnace was cooled to ambient temperature at the rate of 10 °C min^{−1}. The resulting TR-PBO films are denoted as TR-PBO_{temperature} (°C). For example, TR-PBO₄₀₀ means a TR-PBO film obtained after the thermal treatment at 400 °C. Before treated in acids, each membrane was kept in a desiccator to be isolated from any moisture sources.

2.4. Acid-impregnation of TR-PBO membranes

TR-PBO membranes were doped by immersing them in 10 M HCl, HNO₃, H₃PO₄, and HPF₆ solution at room temperature for one day. The increase in the weight of the acid-doped membranes is associated with both water and dopant molecules. In order to minimize the effect of water uptake, acid-doped TR-PBO membranes were sufficiently dried at 110 °C in vacuum until their weights reached unchangeable levels. The acid uptake was defined as the mole number of acid molecules per benzoxazole unit using Eq. (1).

$$\text{Acid uptake [mol.\%]} = \frac{W_{\text{dopant}} / MW_{\text{dopant}}}{(W_{\text{polymer}} / MW_{\text{repeating unit}})} \times 100 \quad (1)$$

where W_{dopant} and W_{polymer} are the weight of an acidic dopant and a basic polymer, respectively. MW_{dopant} and $MW_{\text{repeating unit}}$ denote the molecular weight of the dopant and the polymer repeating unit. The acid-doped membranes were washed in methanol for three days to remove “free acids,” and dried at 80 °C in vacuum [16]. The

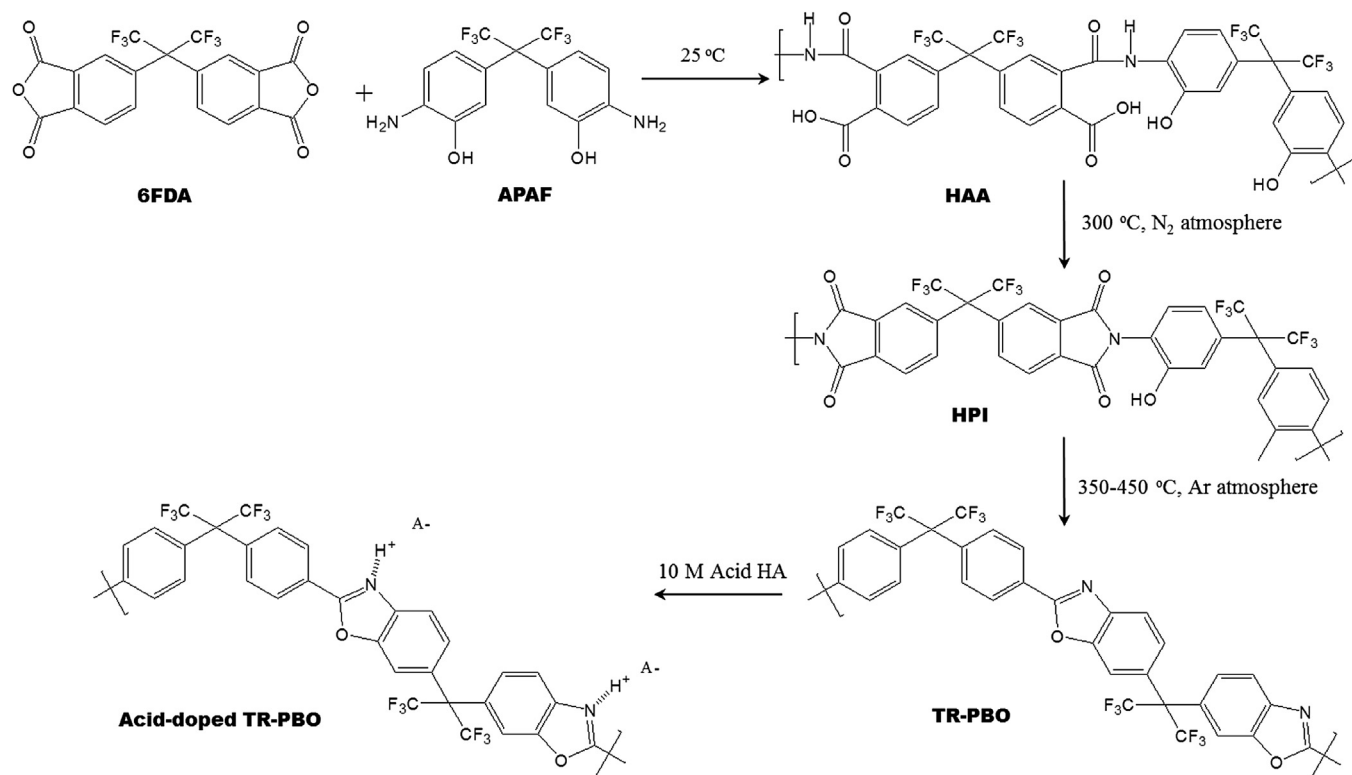


Fig. 1. Preparation scheme of HAA, HPI, TR-PBO, and acid-doped TR-PBO. Here, the counter-anion (A^-) of acidic dopant HA includes Cl^- , NO_3^- , H_2PO_3^- , and PF_6^- .

remaining acids in the membranes were regarded as “bonded acids.” This method was based on the assumption that the complete dissolution of “free acids” and the removal of methanol were accomplished.

2.5. Polymer and membrane characterization

The water uptake of the thermally treated membranes was measured using a dynamic vapor sorption analyzer (DVS-1000, Surface Measurement System Ltd, London, UK) under 90% relative humidity (RH) at $25\text{ }^{\circ}\text{C}$. The FT-IR spectra of the membranes were measured using Thermo Nicolet Magna IR 760 spectrometer (Madison, WI, USA) in the range of $4000\text{--}400\text{ cm}^{-1}$. The X-ray photoelectron spectroscopic analysis (XPS) was carried out to confirm the acid-impregnation in the membranes using the Multilab ESCA 3000 instrument (Thermo VG Scientific, East Grinstead, U.K.) under a high vacuum of 10^{-9} to 10^{-10} torr.

The proton conductivity (σ , S cm^{-1}) of the acid-doped membranes was obtained from Eq. (2) with the ohmic resistance (R_s , Ω) measured using four-point probe AC impedance spectroscopic method in the temperature range from 90 to $130\text{ }^{\circ}\text{C}$ at 28% RH.

$$\sigma = l / (R_s \times S) \quad (2)$$

where l is the distance between the reference electrodes, and S is the cross-sectional area of the membrane sample. For a precise impedance measurement, the membrane coupon was installed on a four-electrode system in a thermo- and hygro-controlled chamber which is connected with an electrochemical interface (Solartron 1287, Solartron Analytical, Farnborough Hampshire, GU14, ONR, UK) in combination with an impedance/gain-phase analyzer (Solartron 1260) [26]. Prior to the measurement, the hygrometer was calibrated using the standard saturated salt solution with well-

known water activity at a certain temperature [27]. The temperature dependency on proton conduction through the acid-doped membranes was determined using Arrhenius equation of Eq. (3).

$$E_a = -RT \ln \sigma \quad (3)$$

where, E_a (kJ mol^{-1}) and R is the activation energy and the gas constant ($8.314\text{ kJ (mol K)}^{-1}$), respectively.

The thermo-oxidative stability of the acid-doped membranes was monitored with a TGA 2050 thermogravimetric analyzer (TA instrument, New Castle, DE, USA), while 1) increasing measurement temperatures from 50 to $200\text{ }^{\circ}\text{C}$ at the heating rate of $10\text{ }^{\circ}\text{C min}^{-1}$ and 2) maintaining a constant temperature of $200\text{ }^{\circ}\text{C}$ in a 60 mL min^{-1} air sweep gas.

3. Results and discussion

The imide ring structure of HPI was completely formed after thermal imidization of HAA at $300\text{ }^{\circ}\text{C}$, as shown in FT-IR characteristics peaks (Fig. 2) such as symmetric (b, 1788 cm^{-1}) and asymmetric stretching C=O vibration (c, 1720 cm^{-1}). The HPI structure containing hydroxyl groups began to be converted into an asymmetric benzoxazole structure after thermal treatment at $350\text{ }^{\circ}\text{C}$. The thermal rearrangement was identified with stretching vibration peaks of benzoxazole rings at (d) 1480 cm^{-1} and (e) 1058 cm^{-1} . The broad hydroxyl groups (a, $2950\text{--}3600\text{ cm}^{-1}$) disappeared in TR-PBO_450, indicating that a complete thermal conversion was accomplished.

This thermal transformation resulted in cavity formation derived from random chain conformation. The cavity features were highly dependent on the thermal rearrangement temperatures. The average cavity diameter increased to $\sim 4\text{ \AA}$ and the cavities became interconnected as the applied temperature increased up to $450\text{ }^{\circ}\text{C}$.

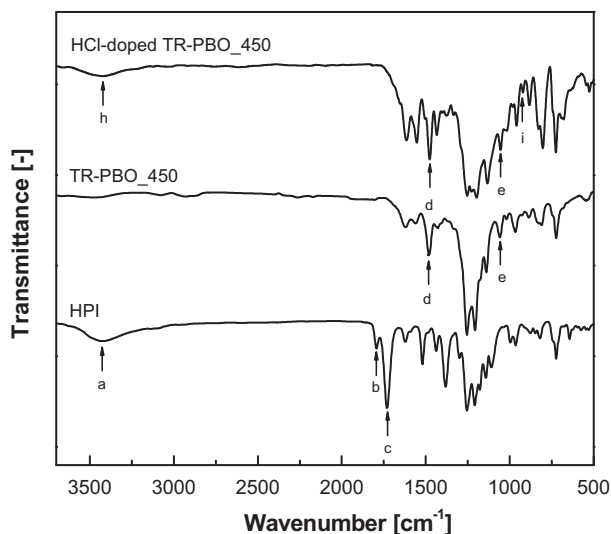


Fig. 2. FT-IR spectra of HPI, TR-PBO_450, and HCl-doped TR-PBO_450.

[25]. The relatively large cavities (average size = $\sim 9 \text{ \AA}$) with a small portion also coexisted, adjoining the small cavities in the hourglass shape. The cavity fraction of TR-PBO_450 (~ 0.38) with a high BET surface area (e.g., $535 \text{ m}^2 \text{ g}^{-1}$) reached to the level similar to most open zeolites ($0.47\text{--}0.5$ [28]). The increase in cavity fraction was also confirmed by measuring water vapor sorption content as a function of thermal treatment temperature. Water vapor uptake in Fig. 3 improved as the thermal rearrangement was carried out. The water molecules were believed to be absorbed primarily in the microporous structure of TR-PBO.

Acid-doped TR-PBO was made by immersing the basic polymer in acid solutions (e.g., 10 M HCl) instead of water vapor. The acid-doping into TR-PBO was verified by both FT-IR and XPS spectra in Figs. 2 and 4, respectively. The acid dopants with hygroscopic properties can absorb water molecules in the atmosphere to some extent. Thus, it is inevitable that the characteristic peak of water (h, $3200\text{--}3600 \text{ cm}^{-1}$) was observed in HCl-doped TR-PBO_450. The vibration peak assigned as chlorinated ion (Cl^-), HCl counter anion,

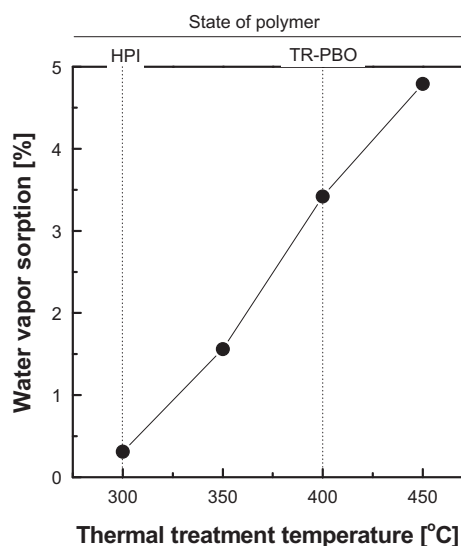


Fig. 3. Water vapor sorption change of membrane materials obtained as a result from thermal conversion of HPI into TR-PBO.

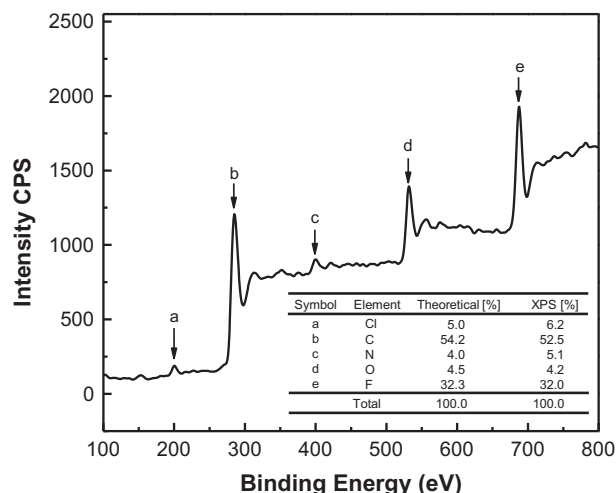


Fig. 4. XPS spectrum of HCl-doped TR-PBO_450 and its elemental composition.

was detected at (i) 920 cm^{-1} , since protonated TR-PBO would be in a single phase complex with the counter anion. The existence of Cl^- ions was also observed at 198 eV of XPS spectrum (Fig. 4) where $2p_{3/2}$ binding energy of the anions was consistent with that of alkaline chloride [29]. The elemental composition of HCl-doped TR-PBO_450 based on XPS analysis corresponded well to that of TR-PBO containing one HCl molecule per repeating unit. The impregnation using other acids such as HNO_3 , H_3PO_4 and HPF_6 was confirmed in the same manner.

The acid-doping effect on thermal treatment temperature chosen to prepare basic polymer matrices including HPI and TR-PBO is shown in Fig. 5. In addition to benzoxazole rings with basic —C=N— groups, the electron-donating imide rings in HPI, TR-PBO_350, and TR-PBO_400 can be impregnated with strong acids. Simultaneously, some portion of HPI can be decomposed via chemical etching during the acid treatment, as observed in other polyimides [30]. The weight loss in HPI was observed after the treatment in 10 M HCl selected as one of acidic dopants, which

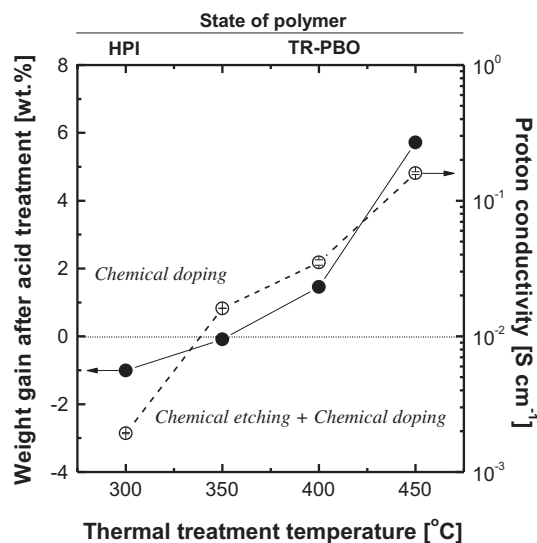


Fig. 5. The acid-treatment effects of HPI and TR-PBO membranes prepared after thermally treated at a certain temperature for 1 h. All the basic membranes were immersed in 10 M HCl solution for one day. Their proton conductivity was measured at 130°C and 28% RH.

means that the chemical decomposition was more predominant than the acid doping in the polyimide system. On the other hand, the thermal treatment of HPI at increasing temperature to 450 °C led to an increase in the portions of chemically stable benzoxazole moieties, which depressed the reduction of initial weight associated with the acid etching. Consequently, the total weight in HCl-treated TR-PBO membranes increased to 5.72 wt.% via a synergistic effect with improved cavity fraction. The weight gain in HCl-treated TR-PBO_450 is numerically converted into acid uptake value of 107.6 mol.%, assuming that there may be no chemical decomposition in TR-PBO_450 with excellent acid resistance. The calculated doping level is almost in accordance with that on the basis of XPS analysis (see Fig. 4). Moreover, proton conductivity of all the basic membranes increased rapidly from 1.9×10^{-3} to 1.6×10^{-1} S cm⁻¹ in proportion to the applied thermal treatment temperature used for chemical conversion from HPI to TR-PBO.

Table 1 shows the uptake level of TR-PBO_450 to acidic dopants with different physico-chemical properties such as acidity and the thermochemical radii of counter ions. The acid doping was largely influenced by the counter ion size of acidic dopants rather than their acidity. The doping level decreased with increasing dopant anion size in order of Cl⁻, NO₃⁻, H₂PO₄⁻, and PF₆⁻. In other words, the small dopants were absorbed into TR-PBO_450 with a relatively high acid uptake. Note that the thermochemical diameter of Cl⁻ and NO₃⁻ is similar to or smaller than the average size of small cavities with a large portion in TR-PBO_450.

Acid uptake of basic membranes (e.g., PBI film), which is known as a key parameter to determine proton conduction properties in acid–base complex systems, depends on both dopant concentration and immersion time in the solution. When a highly concentrated acid solution is used, the doping time is shortened [16]. This trend is more significantly observed in the porous membranes [31]. The HCl doping level of TR-PBO_450 is exhibited as a function of the immersion time in Fig. 6. The HCl uptake rate was fast enough to reach an equilibrium doping level within 3 h. The rapid acid impregnation may originate from both microporous structure of TR-PBO and a high HCl concentration. It is interesting to compare the HCl uptake with that of PBI (e.g., poly [2,2'-(*m*-phenylene)-5,5'-bibenzimidazole]) as a reference treated under the same acid conditions. From the chemistry point of view, PBO (pK_a = ~1.18) has reactivity to acidic dopants lower than PBI (pK_a = ~5.5), because oxygen atoms in PBO prohibits the delocalization of electrons owing to their electronegativity higher than nitrogen atoms in PBI, and weakens the electron-donating effect of their lone pair electrons. Thus, the acid affinity to TR-PBO was expected to be lower than that of PBI with relatively high basicity. HCl doping level in TR-PBO_450, however, was about two times higher than 54 mol.% of PBI. It is likely to be attributed to

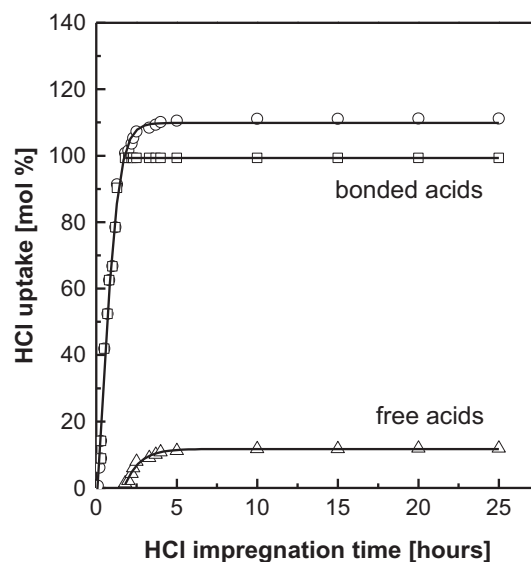


Fig. 6. The total acid uptake (circles), bonded acid contents (squares) and free acid contents (triangles) into TR-PBO_450 membrane as a function of the impregnation time in 10 M HCl solution at room temperature.

the cavity characteristics of TR-PBO_450. In case of other acids, the times taken to equilibrium doping levels were not largely different.

Similar to water as a proton transport media in sulfonated polymers [32], acidic dopants in basic polymers such as PBI and PBO can be classified into free acids or bonded acids according to the interaction with the polymer matrices. The free acids are not closely bound to the polymer matrices and exhibit physical behaviors like bulk acids. Meanwhile, bonded acids are tightly bound to the polymer matrices and are not easily removed even after methanol treatment. During acid treatment, HCl molecules began to preferentially form strong interactions with TR-PBO_450. After the bonded acids were mostly saturated within 2 h, additional free acids seemed to be absorbed. The amount of the fully saturated bonded acids was about 100 mol.% and much higher than that of the free acids. It would make it difficult for most of HCl dopants to leach out even during MT/LH PEFC operation.

The proton conductivity of acid-doped basic polymers is highly affected by acid–base pairs, acid-doping level, acidity of dopants, and measurement temperature and humidity. Protons in acid–base complex systems are transported via hopping mechanism, following Arrhenius law, where protons form and break hydrogen bonds with proton acceptors (i.e., the counter anions of acidic dopants) [33–35]. The influence of acidic dopants on proton conductivity was investigated with TR-PBO_450 after treated in 10 M solutions at the ambient temperature for 3 h. PBI membranes treated under the identical acid conditions were used for comparison. Proton conductivity of acid-doped PBI and TR-PBO_450 membranes is shown as the function of temperature under a fixed humidity of 28% RH in Fig. 7. The proton conductivity increased at the elevated temperatures, regardless of acidic dopant–basic polymer pairs. The proton conductivity values of HCl- and H₃PO₄-doped PBI membranes were 40–70% lower than those of TR-PBO_450 counterparts. Their activation energies (E_a = ~65 kJ mol⁻¹) were superior to those of the corresponding TR-PBO (E_a = 57–63 kJ mol⁻¹), which were about three times higher than values (E_a = 18–25 kJ mol⁻¹) reported in the literature [36]. Those electrochemical properties may be attributed to insufficient acid-impregnation to an equilibrium level (e.g., 560 mol.% per repeating unit of PBI).

Table 1
Basic properties of acidic dopants, and the acid and water uptake of acid-doped TR-PBO_450.

Dopant	Formula weight [g mol ⁻¹]	Acidity [pK _a] ^a	Counter anion	Anionic radii [nm] ^b	Acid uptake [mol.%]	Water uptake ^c [mol.%]
HCl	37	-7.0	Cl ⁻	0.168 ± 0.019	107.6	1.56
HNO ₃	63	-1.3	NO ₃ ⁻	0.200 ± 0.019	38.2	0.58
H ₃ PO ₄	98	2.2	H ₂ PO ₄ ⁻	0.213 ± 0.019	33.5	0.51
HPF ₆	146	-1.6	PF ₆ ⁻	0.242 ± 0.019	21.9	0.34

^a The dissociation constants of inorganic acids [46].

^b The anionic thermochemical radii of ions in salt type MX (1:1) [47].

^c Derived from the difference of TR-PBO_450 weight obtained after 10 M acid treatment at room temperature for two days and after drying at 110 °C under vacuum.

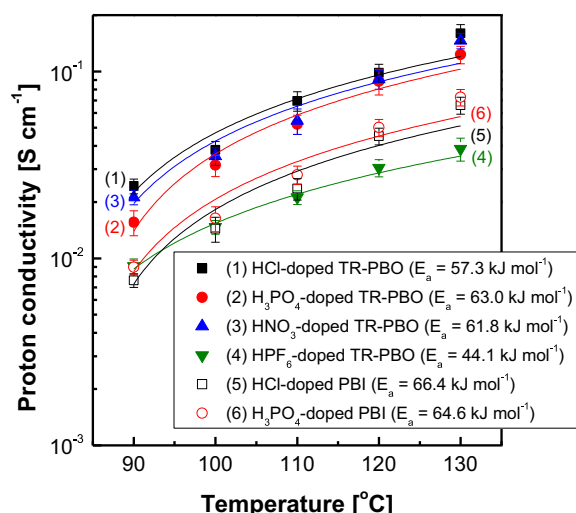


Fig. 7. Proton conductivity of acid-doped PBI and TR-PBO_450 as a function of measurement temperature and their activation energy.

The proton transport through the TR-PBO_450 membranes was more associated with the acid doping levels rather than dopant acidity. When highly acidic HCl with the smallest anionic radius was used as a dopant, the resulting TR-PBO_450 membrane showed the fastest proton conduction under the measurement conditions. On the other hand, HPF₆-doped TR-PBO_450 exhibited the lowest proton conductivity. Note that the doping level of HPF₆ was lower than any other acid owing to its relatively large anionic radius, although HPF₆ is more acidic than HNO₃ and H₃PO₄. Most of acid-doped TR-PBO membranes, except HPF₆ treated one, showed unexpectedly rapid proton conduction even at the anhydrous state (e.g., >0.1 S cm⁻¹ at 130 °C). It may disclose that cavity characteristics including size and connectivity play an important role in determining the proton conduction through acidic medium within TR-PBO membranes.

MT/LH-PEFC membranes should be thermally stable in the fuel cell operation temperature ranges. No severe weight losses derived from the decomposition under the thermo-oxidation conditions were found in the TGA thermograms of HCl-doped TR-PBO_450 (Fig. 8). Similar trends were observed in TR-PBO_450 membranes treated in other acids. This means that acid-doped TR-PBO_450 membranes have excellent resistance to thermal oxidation.

Another vital factor in designing acid-doped basic polymers is physico-chemical preservation of acidic dopants within the polymer matrices. Minimizing acid leaching is directly linked with improved electrochemical sustainability of the resulting membranes. The proton conductivity changes of PBI and TR-PBO_450 containing HCl as a dopant in repeated heating and cooling cycles between 90 and 130 °C is shown in Fig. 9. The measurement interval was 45 min at each temperature. HCl-doped PBI had a relatively rapid reduction of proton conductivity even within a few cycles as a result from HCl leakage even at a low humidity of 28% RH. On the contrary, HCl leakage was alleviated in the TR-PBO_450, since the reduction rate of proton conductivity was relatively slow. Note that proton conductivity in the 20th cycle is not largely different from those in initial cycles. The excellent resistance to acid leaching may be attributed to peculiar cavity characteristics: the small cavities with a narrow distribution play a role in molecular cage to hinder acidic dopants from leaching out. The acid preservation property was also observed in TR-PBO_450 membranes doped with other acids, although the tolerance to acid leaching was more significant when HCl was used.

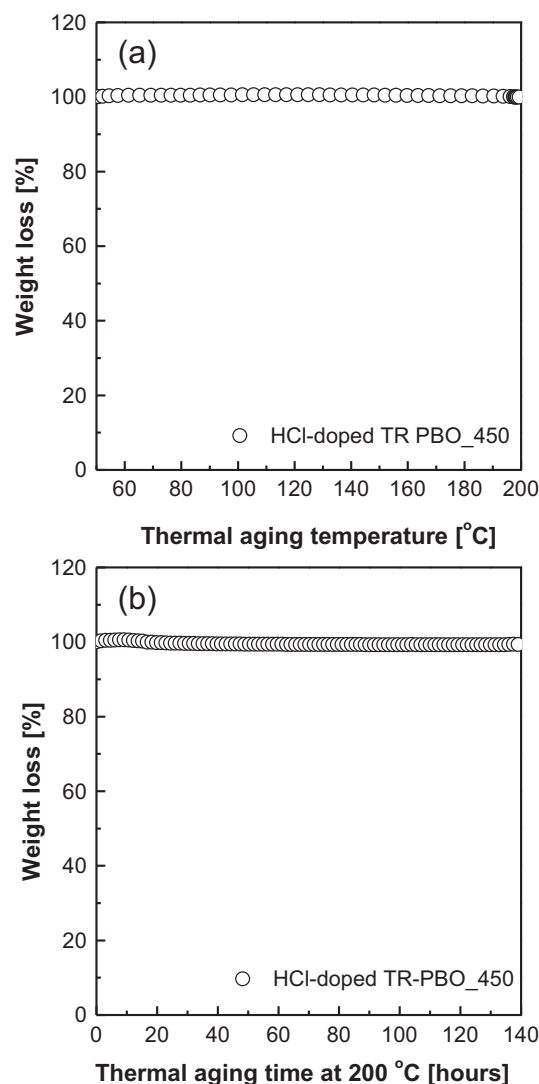


Fig. 8. Thermo-oxidative resistance of HCl-doped TR-PBO_450 observed when aged (a) in MT/LH PEFC operation temperature ranges from 50 to 200 °C, and (b) under an isothermal condition. The applied humidity was 28% RH. The membrane sample was obtained after impregnated in 10 M HCl for 3 h.

The acid-doped TR-PBO_450 membranes look like promising candidates for MT/LH polymer electrolytes owing to their high proton conductivity, and excellent tolerance to thermo-oxidation and acid leaching. The membrane system, however, should satisfy some requirements via our future works: 1) hydrogen barrier property, 2) mechanical toughness, and 3) MEA fabrication. The hydrogen permeability (kinetic diameter of hydrogen = 0.289 nm), which was measured with a high-vacuum time lag method at a feed pressure and a temperature of 14.7 psig and 25 °C, depends on the applied thermal rearrangement temperatures and the types of dopants. The hydrogen permeability of TR-PBO increased from 61 to ~2900 barrer, as thermal rearrangement temperature increased from 300 to 450 °C [37]. High hydrogen permeability of TR-PBO_450 was reduced after treated with acidic dopants, particularly with a relatively large anionic radius (e.g., 30 barrer in HPF₆-doped TR-PBO_450 [25]). Its hydrogen permeability, however, is still higher than those (e.g., ~8 barrer in fully hydrated Nafion 112 under a similar measurement condition [38]) of other fuel cell membranes. Hydrogen barrier property of TR-PBO may be improved by controlling cavity characteristics of TR-PBO via the use

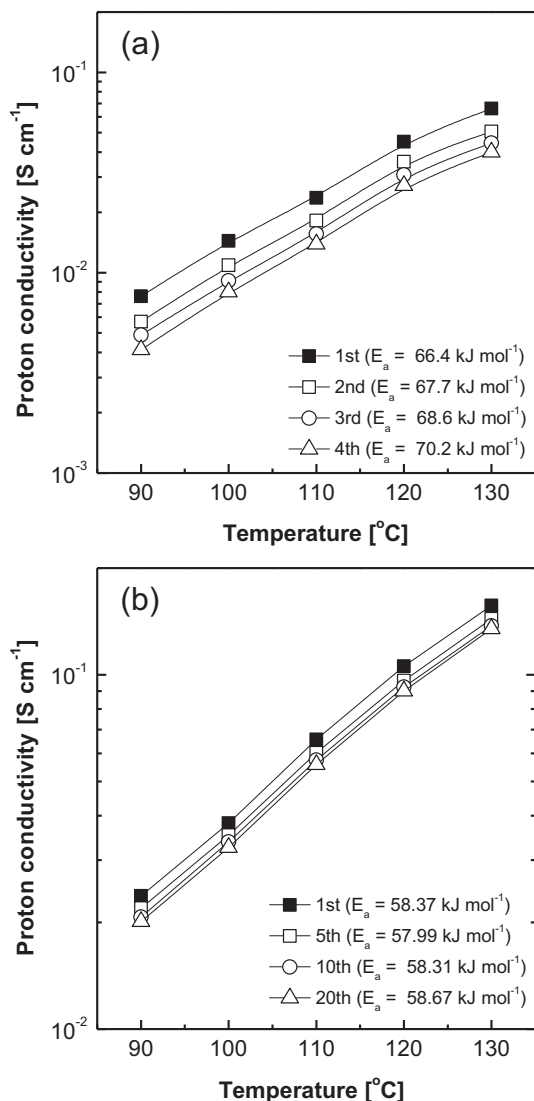


Fig. 9. The proton conductivity reduction derived from HCl leakage from (a) PBI and (b) TR-PBO (applied humidity = 28% RH). All membranes were treated in 10 M HCl solution for 3 h before measuring their proton conductivity.

of different synthetic routes [39] and polymer precursors with diverse chemical architectures [37,40–44].

Mechanical properties of TR-PBO can be strengthened by lowering a thermal rearrangement temperature. When TR-PBO membranes were obtained at 400 °C, for example, their tensile strength and elongation at break were about two times higher than ones treated at 450 °C [43]. The electrochemical PEFC evaluation has not been carried out yet, since membrane-electrode assemblies based on acid-doped TR-PBO membranes need a catalyst binder made up of TR-PBO or its derivatives for forming electrodes with a low interfacial resistance. Simultaneously, fundamental studies associated with possible electrochemical effects of acidic dopants on electrodes composed of Pt and carbon materials (e.g., graphite) with different shapes and sizes should be achieved to maximize PEFC performances of acid-doped TR-PBO membranes. One good example is observed in aqueous solutions containing chloride (Cl⁻) ions where Pt particles are often poisoned, showing undesirable corrosion and degradation, as a result from easy adsorption of Cl⁻ ions on their surface [45]. Nevertheless, the concept on the use of basic polymers with cavities, whose size is similar to or little bit

larger than those of counter anions of acidic dopants, for stable acid impregnation is meaningful in designing highly proton-conductive polymer electrolytes for MT/LH-PEFCs.

4. Conclusions

TR-PBO membranes with controlled cavity characteristics are prepared via thermal rearrangement of a hydroxyl-containing polyimide (HPI) precursor from 350 to 450 °C and used as basic polymer matrices for acid impregnation in 10 M acid solutions at 25 °C. The formation of acid–base complexes in acid-treated TR-PBO is confirmed by FT-IR and XPS measurements. The acid-doping level in TR-PBO is improved as the thermal treatment temperature increases. This trend is attributed to an enhanced portion of chemically stable benzoxazole moieties and an increase in the fraction of cavities used as acid-doping sites. The acid uptake of TR-PBO_450 is inversely proportional to thermochemical radius of counter anion of each dopant. When doped with acids with anionic size similar to or smaller than average cavity size, the TR-PBO_450 exhibits a relatively high doping level. Acid impregnation into microporous TR-PBO_450 is fast enough to reach an equilibrium doping level within a shorter period of time than that taken in PBI. Most of acids doped in TR-PBO are strongly bound to the polymer matrix even after treated in methanol. The proton transport is influenced by the acid doping level rather than dopant acidity. The maximum proton conductivity at 130 °C and 28% RH is observed in HCl-doped TR-PBO_450 with the highest acid uptake (e.g., 1.6×10^{-1} S cm⁻¹ after HCl impregnation). Although HPF₆ is more acidic than HNO₃ and H₃PO₄, low acid uptake derived from its relatively large thermochemical radius causes TR-PBO_450 to have the lowest proton conductivity. TR-PBO_450 membranes treated with acidic dopants, except HPF₆, presents proton conduction behavior faster than corresponding PBI membranes under an MT/LH condition. The unexpectedly high proton conductivity may be associated with cavity size and its connectivity in TR-PBO_450. Finally, acid-doped TR-PBO_450 membranes show outstanding resistance to thermo-oxidative decomposition in an MT/LH-PEFC operation temperature range. Severe acid leaching and then critically reduced proton conductivity are not observed in the acid-doped TR-PBO_450 membranes when compared with PBI counterparts.

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